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(54) Title: TEXTILE PRINTING SUBSTRATE

(57) Abstract: A textile substrate is treated with a composition having a dye fixing agent and an ink receiving agent, for the subsequent printing with an ink jet printer. The dye fixing agent includes a reactive amino compound which chemically bonds with the textile substrate. A resin binder can also be used where the dye fixing agent does not provide an adequate bond to the textile substrate, a resin binder can be used to bond with the textile substrate and the dye fixing agent can bond with the resin binder. The ink receiving agent comprises inorganic particles such as behemite, alumina or silica gel.

TEXTILE PRINTING SUBSTRATE

Background

The present invention generally relates to the printing of textiles.

Due to the many various types of textile substrates that printing is performed on, and the many various types of printing inks, is often difficult to obtain consistency in the quality of the print between printed textiles. These complications are magnified by the difficulty of obtaining a quick drying, sharp focused print on textile materials in general. Additionally, pigment based inks require additional binders, and most dyes require an additional dye fixing process when printing on a textile.

Therefore, there is a need for materials that allow the printing on various different types of textiles with various different types of printing inks thereon, enhance the fast pickup of the ink on the textile and help in obtaining sharp well defined patterns, and assist in the reduction of the need for special binders or fixing processes for printing on textiles.

Detailed Description

The present invention is directed to the treatment of a textile substrate for the subsequent reception of a printing ink, such as ink from an ink jet printer. In one embodiment, the treatment of the present invention includes the placement of a treatment of a dye fixing/receiving composition on the surface of the textile substrate which is to receive the printed ink, prior to placement of the printing ink on the textile substrate. The dye fixing/receiving composition generally includes a dye fixing agent and an ink receiving agent. In one embodiment, the dye fixing/receiving compound can include a compatible resin binder. Additional additives can be used with the dye fixing/receiving composition, such as whitening agents, antimicrobial agents, light stabilizers/UV absorbers, and lubricants. The textile with the dye fixing/receiving agent thereon can also be subjected to a mechanical treatment to improve the flexibility and surface touch of the treated textile. In another embodiment, the treatment of the present invention includes the placement of a UV absorber on the surface of the textile substrate which is to receive the printed ink, prior to placement of the printing ink on the textile substrate.

The textile substrate contributes to whiteness, texture, and physical porous structure for holding the ink. The textile substrate can be a knit, woven, nonwoven, or similar type textile. In one embodiment, the textile substrate is a tight woven fabric. It has been found that textile substrates formed of dull white opaque textured or spun yarns provide a good substrate for the present invention. For example, tightly woven fabrics from cotton staple yarns provide opacity and absorbency that assists in the functions of the treatment of the textile substrate. The material of the textile substrate can be synthetic, natural, or regenerated. In most cases, it is the treatment that receives a majority of the dyes in the ink. It has been found that the present invention with a bright white substrate provides better brightness and contrast for the resulting image on the textile. The surface touch of the textile substrate, before and after treatment and printing, can be greatly improved by surface sanding, especially by the use of fine grade sanding media prior to treatment of the substrate. Sanding with fine grid sanding media, such as fine diamond, gives the fabric surface fine short fibers, which is responsible for smooth and soft touch. In one embodiment, the hairiness of the textile substrate was measured with average fiber heights of about 0.15 millimeters or greater, and an average level of about 0.3 – 0.8 millimeters was preferred. In these hairiness levels, the present inventors have discovered that the inkjet printing process or print quality are not effected.

The dye fixing/receiving composition of the present invention includes a dye fixing agent and an ink receiving agent. In one embodiment, the fixing agent has a molecular weight of at least about 1000. The fixing agent of the present invention comprises reactive amino compounds of a highly cationic nature. A preferred reactive amino compound is a compounds having a high positive charge density (i.e., at least two (2) milliequivalents per gram). Reactive amino compounds that can be used in the present invention include compounds containing at least one primary, secondary, tertiary, or quaternary amino radical. Additionally, the reactive amino compounds can contain a reactive group that is capable of reacting with the textile substrate or resin binder to form a bond thereto. Examples of a reactive group include epoxide, isocyanate, vinylsulphone, and halo-triazine.

Ink receiving agents of the present invention are inorganic particles that receive the ink through adsorbancy or absorbancy. In one embodiment, the particle size of the ink receiving agent is equal to, or less than, about 10 microns. In another

embodiment, the particle size of the ink receiving agent is equal to, or less than, about 3 microns. In yet another embodiment, the particle size of the ink receiving agent is equal to, or less than, about 1 micron. Examples of ink receiving agents of the present invention include silica, silicate, calcium carbonate, aluminum oxide, aluminum hydroxide, and titanium dioxide.

In particular, it has been found that Bohemite alumina and silica gel work well in the present invention, especially silica gel particle that have been treated to carry a cationic charge. In the case of silica gel particles, alumina surface coating and cationic silane surface modification are preferred. It is believed that the microporous nature of the bohemite alumina and silica gel allow further physical entrapment of a dye/pigment, such as an anionic dye/pigment, to afford improved wash fastness. In one embodiment, the inorganic particles have a porosity with a pore diameter from about 10nm to about 200nm.

In most formulations, the cationic charge from cationic reactive amino compounds is much greater than the cationic charge present on the inorganic particles. Therefore the mere presence of relative minor cationic charge on the inorganic particle would not significantly improve the dye/substrate interaction through cationic-anionic charge interaction. It is combination of highly charged reactive amino compound and the microporous inorganic particles that further improves the washfastness of a printed article.

In one embodiment, the fixing agent typically will comprise from about 0.2% to about 20% by weight of the treated textile substrate. In one embodiment, the ink receiving agent typically will comprise from about 0.2% to about 20% by weight of the treated textile substrate. In one embodiment, the dye fixing/adsorbing composition comprises from about 1% to about 10%, by weight, of the treated textile substrate. In another embodiment, the dye fixing/adsorbing composition comprises from about 1% to about 5%, by weight, of the treated textile substrate. Prior to placement on the textile substrate, the dye fixing/receiving composition is preferably in the form of a stable aqueous solution or dispersion.

In the embodiment using a resin binder, the resin binder must be a binder that will have good a bond with the fiber of the textile substrate. The resin binder can be a thermoplastic or thermosetting polymeric binder. It is preferable that the resin binder has a glass transition temperature of below about 40°C. It is also preferred

that the binder be durable when subjected to washing. Examples of resin binders include non-anionic or cationic latices, such as ethylenevinylacetate, acrylic, urethane polymer, polyamide, polyester, and polyvinyl chloride. In one embodiment, the resin binder comprises up to about 10% of the weight of the treated substrate.

5 Whitening agents can include white pigments and optical brighteners. White pigments provide an improved white background for the inks and dyes placed on the textile substrate, thereby increasing the contrast of the image on the textile substrate. Examples of white pigments would include zinc oxide and titanium oxide, and calcium carbonate. Optical brighteners having photo-luminescent properties
10 brighten the background of the textile substrate to provide a greater contrast with the inks and dyes placed on the textile substrate. Examples of optical brighteners could include stybene based materials such as Leucophor from Clariant Corporation.

 An antimicrobial agent inhibits the growth of microorganisms, such as bacteria, fungi, or the like, which can cause discoloring of an image on the textile
15 substrate and/or degradation of the textile substrate itself. The antimicrobial agent can be an additive which is compatible with the cationic fixing agents, and is durable to weathering. Examples of suitable antimicrobial would include polyguanidine, silver zirconium phosphate, and quaternary aminosilane.

 Light stabilizers are materials that contribute to stabilizing the colorants in the
20 printed ink and textile substrate. Examples of light stabilizers could include hindered amines and hindered phenol, such as Cyasorb 3346 by Cytec Industries and Irganox by Ciba Specialty Chemicals.

 UV absorbers are materials that strongly absorb harmful UV radiation, thereby reducing the exposure of the colorants in the printed ink from the harmful UV
25 radiation. In one embodiment, the UV absorber comprises from about 0.1% to about 10% of the weight of the treated textile substrate. Traditionally, it was believed that the UV absorbers needed to be applied with the ink or cover the ink as a post treatment to provide protection. However, a surprising discovery of the present invention is that placement of the UV absorber on the textile before printing of the
30 ink, provides an unexpected result of improved light fastness. Examples of UV absorbers can include benzyltriazoles, hydroxyphenones, and Dihydroxybenzylphenone, such as Tinuvin 1130 by Ciba Specialty Chemicals.

It has been discovered by the present inventors that by incorporation of small amount of lubricating agent, the friction force of a needle going through the treated textile in a sewing process can be greatly reduced. Lubricating agents are materials that significantly reduce surface friction. Examples of suitable lubricating agents would include olefin waxes, polysiloxanes, fatty acids and the derivatives thereof, and the like. The reduction of needle friction with a lubricant can be accomplished with out any adverse effect on the printing quality, or print durability. In fact, the fabric handle or surface touch is not usually affected by the lubricant, while needling resistance is greatly improved.

10 The treatment can be applied to the textile substrate by dipping, coating, spraying, powder coating, hot melt coating, and other similar methods. The treatment can be applied to the textile substrate in a single application, or multiple applications. Additionally, the various components of the treatment can be applied together, in particular groupings, or individually. In one embodiment, the treatment is applied to the substrate textile by impregnation or coating, which is then followed by a drying process.

In the embodiment of the treatment having reactive amino compounds, the drying process is typically conducted under an elevated temperature to activate the reactive amino compounds of the dye fixing agent for bonding with the textile substrate and/or the resin binder. An elevated temperature for the drying process is a temperature that accelerates the evaporation of solvents in the treatment and the reaction of the reactive amino compound with the substrate and/or the binder. Typically, an elevated temperature for the drying process would be from about 100°C to about 150°C.

25 The present inventors have discovered that a water fast and wash durable print can be obtained with a high and durable cationic charged density on the fabric. Cationic charge density is measured by the moles of cationic charges bound to the textile substrate per unit area. It is believed that higher charge densities provide more anchoring sites for fixing anionic colorants to the fabric. The present inventors have found that a charge density of at least about 2meq/m² provides a satisfactory charge density for the present invention.

Fabrics treated with charged materials and inorganic particles can be stiff and harsh to touch, which is undesirable. The present inventors have found that the

flexibility of the treated textile can be greatly improved by a mechanical treatment, such as intense vibration, stretching, and localized distortion. Surprisingly, no significant adverse effect on printing quality and print durability is observed on textiles that have been treated and then subjected to such mechanical treatment.

5 The designs or images are placed on the treated surface of the substrate. In one embodiment, the design or image is placed on the treated substrate by an ink jet printer, such as the type for home, office, or commercial uses. The printing ink can contain anionic dye and/or anionic pigments. It has been found that the present invention works well when the printing ink contains an acid dye, a reactive dye, a
10 direct dye, or similar anionic colorants. It has also been found that by ironing the print on the textile substrate with or without steam, or by drying the printed article in a home dryer, the color fastness of the printed article may be improved.

 The present inventors have also discovered that certain anionic dyes used in combination the treated substrate give excellent water and washfastness to a printed
15 article. Such anionic dyes are those containing at least 2 net anionic charge on the chromophore moiety on each molecule when fully disassociated in a polar solvent. Preferably, at least one of the anionic charges are provided by a radical from the carboxylic acid group.

 It is believed that the dye fixing agent interacts with the ionic dyes from an ink
20 jet printer ink in a charge type attraction, and that the dye fixing agent of the present invention typically will react with the fiber of the textile substrate to form a chemical bond with the textile substrate. In an embodiment where a resin binder is used, it is believed that the dye fixing agent will chemically bond with the resin binder, which bonds with the textile substrate. It is also believed that the ink receiving agent
25 provides surface area for the ink from the ink jet printer to interact with the dye fixing agent, thereby facilitating the effects of the dye fixing agent. The interaction of the dye fixing agent and the ink receiving agent provide a surprising result in an improved color yield and image wash durability. The use of the dye fixing/receiving composition as the treatment in the present invention, provides a wash durable and
30 crocking resistant print with little, or no, subsequent fixing procedures or chemical treatment.

 The present invention allows well defined pixels to form and facilitates the drying process of the print. The present invention improves the quality of the printed

image while preserving the flexible hand of the underlying textile substrate. The present invention also allows the use of various different types in inks various different types of substrate textiles.

The print exhibits good crocking resistance and water fastness within a few minutes after printing. The article with the image can also withstand repeated laundry cycles with little color fade. It has been discovered that the present invention works well when the pH of the laundry detergent is in the range of from about 4 to about 8.

The present inventors have also discovered that textile substrates treated with the present invention can provide a printed textile with excellent color brightness and print resolution when an aqueous pigment ink is placed on the treated textile substrate by an ink jet printing process. Pigment inks are commonly used to provide an image on a textile due to the superior lightfastness and environmental stability of such inks. However, when the image is placed on the textile with an ink jet printer, the ink jet printer needs an ink with low viscosity and that does not dry up to plug the ink jet nozzles. To meet the needs of an ink jet printer, pigment ink without resin binders are becoming commonly used in ink jet printing processes. However, inks without resin binders typically have poorer rub fastness and washfastness. In order to overcome these characteristics, the prior art has used post-printing lamination or coating to provide a permanency to the print.

Surprisingly, an aqueous pigment ink containing virtually no resin binder can be ink jet printed on a treated textile substrate of the present invention to produce a water fast and weatherable printed image on the treated textile without the use of post-printing lamination or coating. It is believed that the inventive treatment swells when it receives the aqueous ink. It is also believed that this swelling will increase the chances of the interaction between the pigment particles of the ink and highly cationic and porous features of the treatment. As a result, a long-lasting print can be placed on a textile substrate using either a thermal or piezo ink jet printing process without post-printing lamination.

The present invention can be better understood with reference to the following examples:

EXAMPLES 1-3

A treatment mixture containing a reactive dye fixing agent, Kymene 736 (manufactured by Hercules, Wilmington, DE), a inorganic silica particle dispersion, Ludox CL-P (manufactured by W.R. Grace & Co., Columbia, MD), and a ethylene vinylacetate latex binder, Airflex TL -51 (manufactured by Air Products and Chemicals, Inc., Allentown, PA) was made according to the following formula:

	Ludox CL-P	8 parts by weight
	Kymene 736	12 parts by weight
	Airflex TL-51	4 parts by weight
10	Water	76 parts by weight

A small amount of ammonia hydroxide solution was added to adjust the pH to 11.

A woven cotton Poplin substrate (Example 1), a plain woven polyester substrate with textured yarns (Example 2), and a plain woven 50/50 polyester/cotton substrate (Example 3) were separately impregnated with the above treatment solution, passing through nip rolls to get a wet pickup of about 60%. The impregnated substrates were dried in a convection oven at 300°F for 3 minutes.

The treated substrates were printed with solid circles and squares of 3 primary colors (red, blue, yellow) and black using Hewlett Packard DeskJet 932C ink jet printer. The images on each of the treated substrates showed very good sharpness at the edges, with excellent color holdout and no evidence of ink feathering. The printed substrates were then washed in a regular home washer using delicate cycle using Gentle Cycle Woolite neutral detergent following AATCC Standardization of Home Laundry Text Condition (Developed in 1984 by AATCC Committee RA88, and as revised in 1986, 1992, and 1995.). The substrates were then dried in a regular home dryer at low heat for 20 minutes. Very little color loss was observed after the washing. No color bleeding or migration was observed. Color value (CIE L*, a* and b* values) of each of the colors on the printed substrates after one wash and five washes was measured using an X-Rite SP78 Spectrophotometer utilizing the QA Master software for Microsoft Windows Version 1.71 (both manufactured by X-Rite Inc., Grandville, MI). E versus the color printed on a piece of white paper was used to measure the degree of color loss. Wet crocking (AATCC test method 8-1996), and waterfastness (AATCC test method 107-

1997) were also measured on each primary color on the substrates after one wash. The test results are summarized in Table 1 and Table 2.

Table 1
Test Values After One Wash

		Black	Yellow	Red	Blue
Cotton	ΔE vs. paper	2.05	18.41	7.20	8.21
	Wet Crocking*	1	4	4	3
	Water Colorfastness	5	5	5	5
50/50 Cotton/PET	ΔE vs. paper	3.35	26.31	14.17	9.00
	Wet Crocking*	1	2.5	3	3
	Water Colorfastness	5	5	5	5
PET	ΔE vs. paper	2.74	39.27	23.00	12.80
	Wet Crocking*	1.5	3	1.5	2.5
	Water Colorfastness	5	5	5	5

5 * AATCC Grey Scale for Staining

Table 2
Test Values After Five Washes

		Black	Yellow	Red	Blue
Cotton	ΔE vs. paper	0.63	5.67	5.25	4.96
50/50 Cotton/PET	ΔE vs. paper	8.62	11.20	9.73	9.06
PET	ΔE vs. paper	5.40	14.82	11.73	9.92

* AATCC Grey Scale for Staining

EXAMPLES 4-6

10 Control examples were formed using the same substrates as in Examples 1-3 without treatment, as the corresponding Examples 4-6. The untreated substrates were printed using the same printer with the same prints as in Examples 1-3. A significant ink feathering was noticed on the control example of the polyester fabric, and a small degree of ink feathering was noticed on the control example of the 50/50
15 polyester cotton blend substrate. Lower color yield was observed on all the control examples compared with corresponding treated substrates in Examples 1-3. After

one home wash as described in Examples 1-3, there was very little color remained on the fabric.

EXAMPLE 7

Similar formula as in Examples 1-3 was used, except that Ludox CP-L was not included. The same cotton woven cotton substrate as in Example 1 was treated in the same manner as Example 1. Print quality and color fastness were measured. The color yield of Example 7 was lower and the print was not as wash fast as treated cotton substrate in Example 1.

EXAMPLE 8

Similar formula as in Examples 1-3 was used, except that Kymene 736 was not included. The same cotton woven cotton substrate as in Example 1 was treated in the same manner as Example 1. Print quality and color fastness were measured. The color yield of Example 8 was significantly lower and dramatic color loss was observed after one wash.

EXAMPLE 9

Similar formula as in Example 1 was used, except that 1 part of Reputex 20 (antimicrobial agent manufactured by Avecia Biocides, Wilmington, Delaware) was added to 100 parts by weight of the treatment mixture in Example 1. The treated cotton substrate of Example 1, the untreated cotton substrate of Example 4, and the treated antimicrobial substrate of Example 9 were tested for antimicrobial performance. Antibacteria testing was performed using AATCC test method 100, and the results are shown in Table 3. An antifungal test using ISO 846 Test method was also conducted on these substrates and the results are shown in Table 4. The cotton substrate of Example 9 treated with the antimicrobial showed excellent antibacteria and antifungal performance. *Aspergillus niger* is one of the most common fungus that causes mildew staining. *Chaetomium globosum* is one fungus that can grow on cellulosic material and therefore can biologically degrade and destroy cotton fabric. A treatment containing Reputex 20 therefore can help prevent mildew staining and biological degradation of cotton fabric.

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Table 3

Antibacteria Test Against Staphylococcus

Test Sample	Log Reduction
Example 4 (Without Treatment)	1.37
Example 1 (Treatment w/o Antimicrobial)	0.57
Example 9 (Treatment with Antimicrobial)	4.40

Table 4

Antifungal Test*

5

Test Sample	Aspergillus Niger	Chaetomium Globosum
Example 4 (Without Treatment)	10/10	10/10
Example 1 (Treatment w/o Antimicrobial)	10/10	1/10
Example 9 (Treatment with Antimicrobial)	0/10	1/10

* Number of drops of standard fungus solution showing growth out of 10 drops of inoculum after one week.

EXAMPLE 10

Similar formula as in Examples 1-3 was used, except that 1 part by weight of Sunlife LPS-911 (UV absorber manufactured by Nicca USA, Fountain Inn, South Carolina) was added to 100 parts by weight of the treatment mixture in Example 1. A cotton substrate as described in Example 1 was treated and printed as described for Example 1. Xenon lightfastness (AATCC test method 16-1998) at 20 hours exposure were tested and compared with treated cotton in Example 1 and printed paper subjected to the same exposure. The results of the testing are summarized in Table 5. Lightfastness was improved by using the treatment formula for Example 10 containing UV absorber. It is somewhat surprising as the colorants were applied on top UV absorber treatment. The present inventors believe that some of the UV absorber must have migrated towards the surface and/or the dyes in the printing ink migrate beneath the treatment.

12
Table 5
Light Fastness

Test Sample	Black	Yellow	Red	Blue	Average
Paper	5.0	4.5	2.5	1.5	3.4
Example 1	5.0	1.0	1.0	1.5	2.1
Example 10	5.0	4.0	3.5	2.0	3.6

EXAMPLE 11

5 The following formula, in parts by weight, was used as a treatment on a
woven Poplin cotton fabric:

Epi-rez 6006-w-70 4 parts
(waterborne epoxy resin, by Shell
Chemical Company, Houston Texas)

10	Ancamide 500	4 parts
	Ludox CI-P	10 parts
	Water	82 parts

Epi-rez acts both as resin binder and reactive agent that couples with

15 Ancamide (amino compound containing both primary and secondary amines) to generate a durable amine containing finish. The cotton fabric was treated using this formula in the same manner as described in Example 1, and printed and test in the same manner.

EXAMPLE 12

20 A treatment mixture containing a reactive dye fixing agent, Kymene 736 (manufactured by Hercules, Wilmington, DE), a silane-surface-modified silica gel dispersion, Sylojet 703C (manufactured by W.R. Grace & Co., Columbia, MD), and a ethylene-vinyl acetate latex binder, Airflex TL -51 (manufactured by Air Products and Chemicals, Inc., Allentown, PA), a silicone softener, Dousoft OH (manufactured by
25 Boehme Filatex, Reidsville, NC), and a fluorescent whitening agent, Ultraphor SFN (manufactured by BASF, Charlotte, NC) was made according to the following formula in parts by weight:

	Water	53 parts
	Kymene 736	30 parts
	Airflex TL-51	10 parts
5	Sylojet 703C	5 parts
	Dousoft OH	1.5 parts
	Ultraphor SFN	0.5 parts

A woven cotton fabric (cotton Poplin) substrate was impregnated with the
10 above solution, passing through nip rolls to get a wet pickup of about eighty percent
(80%). The impregnated substrate was dried in a convection oven at 300°F for five
(5) minutes. The treated substrate was printed and tested for washfastness as
described below, and the results are shown in Table 6.

The treated substrate was printed with solid squares of 4 primary colors (red,
15 blue, yellow and black) using a Hewlett Packard DeskJet 932C ink jet printer. The
treated substrate showed very good sharpness at the edges with excellent color
holdout and no evidence of ink feathering. The washing procedure was the same as
used in Examples 1-3, including the drying. This washing process was repeated up
to values of five (5) and fifteen (15) times. Color value (CIE L*, a* and b* values) of
20 each primary color on the printed fabrics after one wash was measured using X-Rite
SP78 Spectrophotometer utilizing the QA Master software for Microsoft Windows
Version 1.71 (both manufactured by X-Rite Inc., Grandville, MI). Delta E (cmc)
versus the color printed on a piece of white paper (Hammermill Inkjet 24 lb. paper
manufactured by International Paper of Memphis, TN) was used to measure the
25 color loss reported in Table 6.

Table 6

Washfastness

Example	Washes	ΔE CMC vs. Hammermill Jet Print 24# Paper			
		Black	Yellow	Red	Blue
Example 12	5	1.54	6.14	3.78	4.23
	15	4.04	8.11	6.36	6.44
Example 13	5	1.51	2.14	2.47	2.23
	15	1.67	5.00	5.68	5.07

- Example 12 was used to test several ink jet dyes by making about a 5% solution in mixture of water and propylene glycol and a solid color circle was inkjet printed using each dye on an unprinted fabric of Example #15 using a thermal inkjet printing head. Waterfastness of the print was tested by soaking the printed circle in small amount of water for 5 days and observe the color bleeding into water and color migration to outside the color circle, and the results are shown below in Table 7.

Table 7

Ink Bleed And Migration

Dye Molecules	Anionic Group On The Chromophore	Net Negative Charge	Bleed Into Water	Color Migration
C.I. Acid red 1	2 SO_3^{1-}	2	Minimal	No Migration
C.I. Acid red 52	One $-\text{O}^+ -$, 2 SO_3^{1-}	1	Significant	Severe
C.I. Acid red 289	One $-\text{O}^+ -$, 2 SO_3^{1-}	1	Significant	Moderate
C.I. Direct Red 227	6 SO_3^{1-}	6	Minimal	No Migration
Pro-Jet fast Red			None Noticeable	No Migration
C.I. Acid yellow 23	2 SO_3^{1-} , One COO^{-1}	3	None Noticeable	No Migration
C.I. Acid blue 9	One $=\text{N}^+$, 3 SO_3^{1-}	2	Slight	Slight
C.I. Direct blue 86	2 SO_3^{1-}	2	Minimal	No Migration

As can be seen in Table 7, dye molecules with more than 2 net negative charges on the chromophor of the molecule give satisfactory water fastness on this inventive highly cationic treated fabric. Dye molecules with carboxylic acid radical, such as Pro-Jet Fast Red and C.I. Acid yellow 23, have superior water fastness.

5

EXAMPLE 13

A treatment mixture was formed of the same components as in Example 12 in the following formula in parts by weight:

	Water	33 parts
	Kymene 736	30 parts
10	Airflex TL-51	10 parts
	Sylojet 703C	25 parts
	Dousoft OH	1.5 parts
	Ultraphor SFN	0.5 parts

15

The above treatment was aplaced on the same woven cotton Poplin fabric substrate as Example 12, in the same manner as Example 12. The washfastness of Example 13 was tested in the same manner as prescribed in Example 12, and the results are reported in Table 6. Suprisingly, as shown in Table 6, increasing the amount of surface-modified inorganic particles of the treatment increases the

20 wastfastness of the treated substrate.

EXAMPLES 14-17

Varying levels of a lubricant (Duosoft OH) were added to the treatment formula used in Example 13, and impregnated onto the same substrate as Example 13 in the same manner to form Examples 14-17. The amount of lubricant added to

25 the treatment formula for each example as specified in Table 8. A test was then performed to determine the amount of force needed to pass a sewing needle through the treated substrates. To determine the force necessary to pass the needle through the treated substrates, a quilting/between hand sewing needle size 10 was mounted facing upward to a AccuForce III force meter manufactured by AMETEK of Largo,

30 FL. Samples of the treated substrates of Examples 14-17 were folded over itself (2-ply) and mounted in an embroidery frame. The folded and treated substrates were then pressed down onto the mounted needle, and the maximum force of

compression to pass the needle through both layers of substrate was recorded as a measure of the ease/difficulty of passing a needle through the fabric and averaged over several trials. The larger the force recorded, the more difficult it is to pass a needle through the fabric. The values for each Example were recorded and are listed in Table 8.

Table 8
Lubricant Levels and Needle Force

Example	Lubricant Level (%)	Needle Force (kg)
Example 13	0	1.3
Example 14	1.0	0.8
Example 15	2.0	0.7
Example 16	3.0	0.6
Example 17	5.0	0.5

As shown in Table 8, addition of a compatible softener can reduce the needle force required to pass a needle through the treated substrate.

EXAMPLES 18-21

A woven Poplin cotton fabric was treated with a treatment mixture containing various amounts of a reactive dye fixing agent, Kymene 736 (manufactured by Hercules, Wilmington, DE), a silane-surface-modified silica gel dispersion, Sylojet 703C (manufactured by W.R. Grace & Co., Columbia, MD), and a ethylene-vinyl acetate latex binder, Airflex TL -51 (manufactured by Air Products and Chemicals, Inc., Allentown, PA), a silicone softener, Dousoft OH (manufactured by Boehme Filatex, Reidsville, NC), a fluorescent whitening agent, Ultraphor SFN (manufactured by BASF, Charlotte, NC), and sufficient 50% caustic (sodium hydroxide) to adjust the pH of the mixture to about 7, as specified below in Table 9.

Table 9

Treatment Mixture (Parts by Weight)

Component	Example 18	Example 19	Example 20	Example 21
Water	23.2	33.4	43.6	53.8
50% Caustic	0.8	0.6	0.4	0.2
Kymene 736	40	30	20	10
Airflex TL-51	7	7	7	7
Sylojet 703C	25	25	25	25
Dousoft OH	3	3	3	3
Ultraphor SFN	1	1	1	1

The woven poplin cotton fabrics for Examples 18-21 were impregnated with the corresponding treatment above, passing through nip rolls to get a wet pickup of about 80%. The impregnated fabrics were dried in a convection oven at 300°F for about 5 minutes.

Samples of each of the Examples were printed with solid squares of 4 primary colors (red, blue, yellow and black) using a Hewlett Packard DeskJet 932C ink jet printer. The printed substrates were then washed in a regular home washer using delicate cycle using Gentle Cycle Woolite neutral detergent following AATCC Standardization of Home Laundry Text Condition (Developed in 1984 by AATCC Committee RA88, and as revised in 1986, 1992, and 1995.). These fabrics were then dried in a regular home dryer at low heat for 20 minutes. This washing process was performed on the treated and printed fabrics for a total of one (1), five (5) and ten (10) times. Color value (CIE L*, a* and b* values) of each primary color on the printed fabrics was measured using an X-Rite SP78 Spectrophotometer utilizing QA Master software for Microsoft Windows Version 1.71 (both manufactured by X-Rite Inc., Grandville, MI) before any washing, and after each washing. Delta E (cmc) versus the color printed on a piece of white paper (Hammermill Inkjet 24 lb. paper manufactured by International Paper of Memphis, TN) was used to measure the color loss, summarized below in Table 10.

Non-printed samples of each of the Examples 18-21 were tested for charge density as explained below, at zero (0) washes, one (1) washing, five (5) washings,

and ten (10) washings, as described above. The data obtained from these measurements is summarized below in Table 10.

To determine the charge density of a substrate, a sample of the substrate is placed in a master solution containing dye molecules of a known charge, the light absorbency of the master solution is measured before and after immersion, the difference in absorbency is used to calculate the amount of dye molecules left on the sample, and the amount of dye molecules left on the sample and the area of the sample are used to calculate the charge density of the substrate before immersion. Two inch (2") by two inch (2") samples of the textile substrate were immersed into a twenty five (25) gram master solution for ten (10) minutes. The master solution was formed using 121.5 mg of cresol red (CAS# 1733-12-6) dye (404.2g/mol. by Aldrich) into 431.0g de-ionized water to make a 0.0282% solution by weight. Samples of the untreated substrate with no washings, and treated substrates with no (0) washes, one (1) washing, and five (5) washings, were each placed in its own master solution. The light absorbency of the master solution for each sample was measured at 434nm in the UV-Visible spectrum before and after immersion of the sample.

The change in light absorbency of the master solution for each sample can be used to determine the amount of dye left on the sample. To determine the amount of dye left on the sample from the master solution, a plot of dye concentration verses light absorbency must be calculated from known dye concentration standards. The dye concentration standards can be created by diluting the master solution. Ten dye concentration standards were created by diluting the master solution, forming ten dye concentration standards with known dye concentrations (w/w) ranging between 5×10^{-6} to 4×10^{-5} . The light absorbency of each dye concentration standard was measured at 434nm in the UV-Visible spectrum, and the concentration and light absorbency data were fitted into Beer's law to form the plot of dye concentration verses light absorbency.

For each of the samples, the difference in light absorbency of the master solution before and after the immersion of the samples is used to determine from the dye concentration verses light absorbency plot the amount of dye left on the sample. Since cresol red dye has only one negative charge per molecule, the amount of cationic charge on the substrate can be calculated based on the number of dye

molecules absorbed over the unit area of the substrate. The charge density of the substrate is then reported in milli-mole/m² or mill-equivalent/m².

Table 10
Washfastness

Test Sample	Washings	Delta E cmc				Charge Density (meq/m ²)
		Black	Yellow	Red	Blue	
Example 18	0	5.31	4.71	2.15	1.69	6.59
	1	4.28	5.32	1.97	3.20	6.48
	5	3.22	6.57	3.93	2.79	2.42
	10	2.92	7.57	6.75	4.40	0.39
Example 19	0	4.52	4.48	2.05	1.65	5.96
	1	3.92	5.64	1.68	3.06	5.44
	5	3.28	6.72	4.21	6.09	0.52
	10	3.12	10.36	7.94	7.57	0.00
Example 20	0	3.81	4.17	1.53	1.70	6.08
	1	3.20	5.61	2.21	2.97	4.09
	5	2.70	7.28	6.25	4.03	0.00
	10	2.22	9.44	6.76	5.99	0.00
Example 21	0	2.56	5.43	2.38	3.41	1.73
	1	1.83	6.31	2.75	5.16	0.18
	5	2.13	13.82	8.15	8.28	0.00
	10	3.90	14.14	12.46	10.69	0.00

EXAMPLES 21-22

A woven cotton Poplin fabric and a polyester Poplin woven fabric treated with the following formula:

	Kymene 736	20 parts
5	Sylojet 703	25 parts
	Airflex TI-51	10 parts
	water	45 parts

A photo-image and a set of black, red, blue and yellow color blocks were printed on each fabric using Epson Stylus Photo 2000P printer with aqueous pigment ink.

10 Printed fabrics were washed once in a home washing machine with added liquid detergent. There was virtually no visible color loss after 1 wash. In comparison, an untreated polyester fabric printed with the same pattern using the same printer, showed dramatic visible color loss after one home wash.

For outdoor weather durability, the printed fabrics were tested in an
 15 accelerated weather-o-meter using SAE J1960 method where fabric samples were exposed to high intensity of UV radiation, and intermitted water spray for 21 days. The amount of exposure in the weather-o-meter is equivalent to 3 month Florida outdoor life. The color changes in terms of ΔE_{CMC} before and after weather-o-meter exposure were measured and summarized below in Table 11. As can be seen from
 20 the results in the table, there was little color change on both printed fabrics. There were no chalking or any other obvious degradation on those printed fabric at the end of 21 day exposure.

Table 11
 Color Change, ΔE_{CMC} After Weather-O-Meter Exposure

Color block	Black	Yellow	Red	Blue
Example 21 (Treated polyester fabric)	4.06	0.99	0.82	4.26
Example 22 (Treated Cotton fabric)	3.57	0.55	0.29	6.52

25

The same treated fabrics were also printed with Mimaki JV-4 wide format printer using aqueous pigment ink without resin binder. The resulted prints have the same water fast, wash fast and weather durable properties.

CLAIMS

1. A textile printing substrate comprising:
 - a textile substrate having a first side and a second side;
 - a dye fixing/receiving composition disposed on the first side of the textile
 - 5 substrate, the dye fixing/receiving composition including:
 - a amino compound forming a chemical bond with the textile
 - substrate; and
 - inorganic particles.
2. A textile printing substrate comprising:
 - 10 a textile substrate having a first side and a second side;
 - a resin binder disposed on the first side of said textile substrate;
 - a dye fixing/receiving composition disposed on the first side of the textile
 - substrate, the dye fixing/receiving composition including:
 - a amino compound forming a chemical bond with the resin
 - 15 binder; and
 - inorganic particles.
3. A printed substrate comprising:
 - a textile substrate having a first side and a second side;
 - a UV absorber disposed on the first side of the textile substrate;
 - 20 an ink disposed on the UV absorber on the first side of said textile substrate.
4. A method of placing an image or design on a substrate, comprising the steps of:
 - coating a first side of a textile substrate with a UV absorber;
 - printing the image or design onto the first side of the textile substrate that has
 - 25 been coated with the UV absorber.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/27759

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B32B 3/00, 5/16, 7/00; D21H 11/00,13/00

US CL :428/206, 311.51

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/206, 311.51

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 6,291,023 B1 (NIGAM) 18 September 2001, col. 10, line 52 thru col. 12, line 67.	1,3,4 ----- 2
A	US 6,342,273 B1 (HANDELS et al.) 29 January 2002.	1-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"N" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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